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Acetylacetone as Chelating Reagent, Extracting Solvent, and Electrolysis Medium for Polarographic Analysis of Uranium (VI)

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DC and differential pulse polarographic determination of uranium(VI) after solvent extraction with acetylacetone has been studied. Acetylacetone(AA) acts as the chelating reagent, the extracting solvent, and the polarographic electrolysis medium. The optimum condition of the aqueous solution for the extraction was pH 7.9 with 0.1 *M* $NaClO_4$. The extracted uranyl acetylacetonate exhibited one well-defined wave of the half-wave potential of -1.5 V *vs.* $Ag/AgClO_4$(AA). The linear calibration curves were obtained in the concentration ranges from 1.0×10^{-5} *M* to 6.0×10^{-4} *M* and from 2.0×10^{-7} *M* to 1.0×10^{-5} *M* for DC and differential pulse polarographic determinations, respectively.

INTRODUCTION

Acetylacetone(AA), a weak acid and dipolar solvent slightly miscible with water, has been used both as a chlating reagent and an organic solvent, particularly in the extraction colorimetric determination of trace elements.[1] Because of its colorration and decomposition by alkalies into acetone and acetate, a coloress liquid of AA could hardly be provided as an organic solvent for extraction colorimetry in the pH range higher than 7. Krishen and Freiser reported on the polarographic determination of uranyl ion separated from bismuth, but the exact composition of the final solution for measurement was not described.[2]

In the previous papers[3,4] the authors had reported on the purification method of AA, the polarographic behaviour of metal acetylacetonates in AA, and its feasibility of the application to the polarographic estimation after solvent extraction with AA. This paper deals with the polarographic determination of uranyl ion by the direct addition of supporting electrolyte into the organic phase. The optimum condition of the aqueous solution for extraction of uranium(VI) was pH 7.9 with the ionic strength of 0.1 *M* $NaClO_4$. The extracted UO_2AA_2 in AA solution exhibited one well-defined wave of the half-wave potential of -1.5 V *vs.* $Ag/AgClO_4$(AA). The determination limit was as low as 2.0×10^{-7} *M* by means of differential pulse polarography.

In the present method, AA is exploited as the chelating reagent, the extracting solvent, and the electrolysis medium simultaneously, in contrast to the conventional extraction polarography where these three are usually different. And moreover, this

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method has another practical advantage of easiness of recovering the solvent once used in the experiment; the recommended procedure had been developed by the authors.[3,4]

EXPERIMENTAL

Apparatus and Reagents

A Princeton Applied Research Polarographic Analyzer Model 174 equipped with a National X–Y Recorder Model VP–6431A was used for the measurements of DC and differential pulse polarograms. The other experimental details were the same as those used in the previous paper[4] unless otherwise noted. The characteristics of the dropping mercury electrode (DME) are m=1.24 mg/sec at a mercury head of 50.0 cm with open circuit in water saturated AA (blank extraction from the aqueous solution at pH 7.9) containing 0.1 *M* tetrabutyl ammonium perchlorate (TBAP).

A Hitachi-Horiba pH Meter Model M–5 with a Horiba Combination pH electrode Model 6028–10T was used to measure the pH of the aqueous solution.

Acetylacetone was purified according to the procedure recommended in the previous paper.[4] TBAP was prepared and purified according to the procedures recommended by one of the authors (T. F.).[9] Uranyl acetylacetonate was prepared by extracting the chlate into benzene from the ammoniacal aqueous solution of uranyl acetate, then dried by evaporating the solvent and recrystallized three times from hot benzene as descrived previously.[2] All other chemicals used were of analytical reagent grade.

Extraction Procedure

The sample aqueous solution containing metal ion, after adjusted the ionic strength with sodium perchlorate and the pH by 1 *M* sodium hydroxide or 0.5 *M* sulfuric acid, was shaken with 15 ml of water saturated AA for ten minutes in the sample tube over the waterbath at 25±0.2°C. The sample solution then allowed to stand still and 10 ml of the upper transparent organic phase was taken out into the polarographic cell and added 342 mg of TBAP to make 0.1 *M* TBAP AA solution. After deoxygenated for ten minutes, the polarogram was measured over the available potential scanning range.

RESULTS AND DISCUSSION

DC Polarograms

The polarograms of uranyl acetylacetonate and the residual current in non-aqueous AA (b and a), and in water containing AA (c, d, and e and a′) are shown in Fig. 1. As can be seen from the residual currents, the accessible potential range are from −0.20 V to −2.25 V *vs.* $Ag/AgClO_4$(AA) in non-aqueous AA (a), and −0.37 V to −2.25 V in water saturated AA (a′).

The half-wave potential and the slope of log-plot of the first wave are −1.55 V and 124 mV, respectively. The height of the first wave increased by the addition of

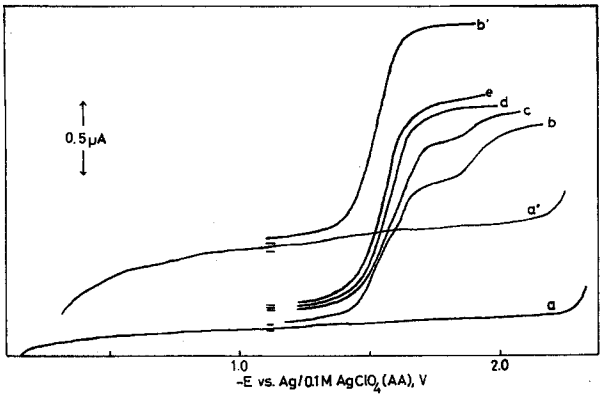

Fig. 1. Polarograms of uranium (VI) in acetylacetone.
(a); residual current and (b); 4×10^{-4} *M* uranyl acetylacetonate in non-aqueous AA with 0.1 *M* TBAP. Uranium waves in (c); 0.3%, (d); 1%, and (e); saturated water containingAA. (a'); residual current and (b'); uranium wave after extraction at pH 7.90

water, whereas that of the second wave decreased and finally disappeared (c and d). With increasing water contents, the first wave inclined to be more well-defined and at last, the apparently one well-defined wave (e) was observed at the potential corresponding to the first wave in non-aqueous medium. That is to say, the rate of disproportionation reaction becomes more rapid by the presence of water. For the extraction polarography of uranium(VI), these behaviour are extremely favourable, *i.e.* in the polarogram of the extract at pH 7.9, uranyl ion exhibited only a single, two electron reduction, and diffusion controlled wave with the characteristics of the half-wave potential of -1.51 V, the slope of log-plot of 99 mV, and the diffusion current constant of 2.90.

Effect of pH, Ionic Strength, and Volume of Aqueous Phase on Extractability

The effect of pH on the extractability of uranyl ion is shown in Fig. 2. As uranyl ion was extracted quantitatively in the pH range between 7.8 and 8.2, the optimum pH of the aqueous phase after equilibrium was chosen at 7.9.

In the extraction colorimetric analysis of uranyl ion, AA could hardly be used as the organic solvent at the pH range higher than 7, because AA is decomposed by alkalies into acetone and acetate, and the decomposition product is very similar in the optical behaviour to UO_2AA_2 chelate.[5,6]

The influence of the ionic strength of aqueous phase on the extractability was shown in Fig. 3. In both regions of the ionic strength lower than 0.02 and higher than 0.2 the extractivity trended to decrease, so that 0.1 *M* $NaClO_4$ was chosen as the optimum ionic strength.

The extractability was also measured by changing the volume of the aqueous solution from 10 ml to 100 ml, containing a given amount of uranium(VI) to form 1.0×10^{-4} *M* solution in the organic phase. As shown in Fig. 4, when the volume of the aqueous phase was three times or more as large as that of the organic phase, the extractability of uranyl ion decreased, because the partition ratio of the chelate is not high enough.[6]

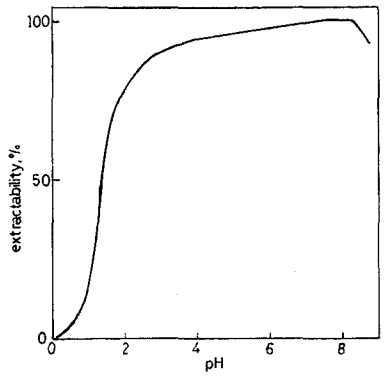

Fig. 2. Effect of pH on extractability of uranium (VI).
1×10^{-4} *M* UO_2^{2+} with 0.1 *M* $NaClO_4$

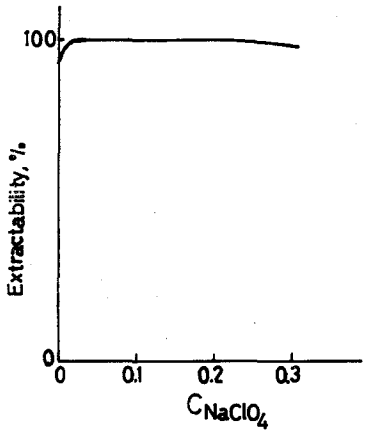

Fig. 3. Effect of ionic strength on extractability of uranium (VI).
1×10^{-4} *M* UO_2^{2+} at pH 7.90

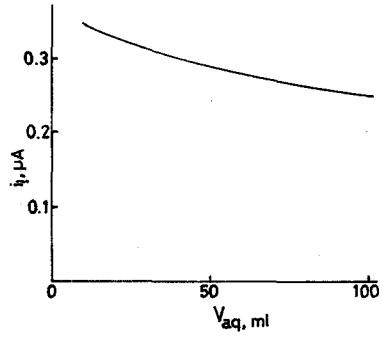

Fig. 4. Effect of volume of aqueous phase on extractability of uranium (VI).
1×10^{-4} *M* UO_2^{2+} with 0.1 *M* $NaClO_4$ at pH 7.90

Effect of Foreign Ions

For the extraction between the equivolume of the organic and the aqueous phases, the diverse ions listed in Table I did not interfere with the determination of uranyl ion unless their concentration exceeded three times as high as that of uranium. The acetylacetonates of the transition metals, such as Mn(III), Pb(II), Fe(III), Cu(II), and Ni(II) showed well-defined waves in non-aqueous AA. Of all these metal ions, however, nickel ion did not exhibit any patent reduction wave in the water containing AA solution.

Lead ion could be masked by EDTA because of the high stability constant of Pb-EDTA. Copper ion interfered at its high concentration. The pre-discharging metal ions such as cobalt(III), manganese(III), and iron(III), whose half-wave potentials were 100 mV or more positive than that of uranium(VI), could be masked with neither EDTA nor potassium cyanide. All anions examined interfered little even at the concentration of seven times that of uranium.

Table I. Effect of diverse ions on the determination of uranium. Uranium(VI) taken; 15 ml of 10^{-4} *M* UO_2^{2+}

Compounds added	[Ion]/[UO_2]	Recovery (%)
NaF	33.3	96.4
$NaHCO_3$	33.3	99.2
Na_2SO_4	28.6	101.2
Na_2HPO_4	33.3	97.4
NaCl	567	98.6
$Na_2B_4O_7$	34.1	98.6
NaI	40.9	99.5
KCN	42.3	101.2
EDTA	19.9	102.2
$NaNO_2$	133.6	—*
$Pb(NO_3)_2$	3.92	97.5
$Co(NO_3)_2$	9.61	97.0
$NiSO_4$	9.86	97.0
$CrCl_3$	6.13	100.6
$MnCl_2$	5.39	100.1
$Ca(NO_3)_2$	14.1	101.5
$ZnSO_4$	12.3	102.8
$FeSO_4$	1.8	69.7**
$Cu(OAc)_2$	1.5	77.2***

* Interfere

** Separable wave, masked with neither KCN, EDTA, nor ascorbic acid.

*** Separable wave

Differential Pulse Polarograms

DC polarographic method is available for the determination of uranyl ion higher than 1.0×10^{-5} *M*. In contrast, differential pulse polarography is suitable for the analysis of uranyl ion lower than 10^{-5}*M*.[7] Fig. 5 shows the typical differential pulse polarogram of 8.0×10^{-6} *M* uranyl ion extracted according to the recommended procedure mentioned above. The dotted line shows the residual current of 0.1 *M* TBAP in AA solution after blank extraction. The peak potential of the uranium wave was -1.48 V *vs.* $Ag/AgClO_4$ (AA).

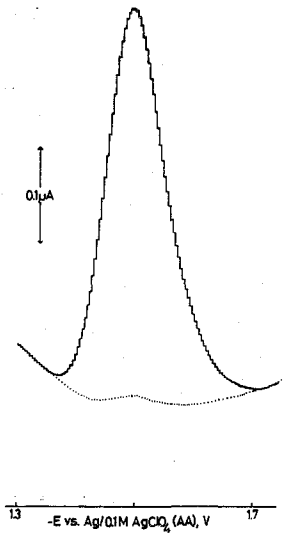

Fig. 5. Typical differential pulse polarogram of uranium (VI) after extraction.

Pulse amplitude; 50 mV, scan rate; 2 mV/sec, current range; 0.5 μA, and drop time; 2 sec, solid line; 8×10^{-6} *M* uranium (VI) wave and dotted line; residual current after extraction at pH 7.90

Calibration Curves

The calibration curves for uranyl ion were obtained after the equivolume

extraction between AA and the aqueous solution containing the different amounts of uranyl acetylacetonate under the optimum extraction conditions. The calibration curve for DC polarographic determination of uranyl ion was linear in the concentration range between 1.0×10^{-5} M and 6.0×10^{-4} M as shown in Fig. 6. A linear calibration curve was also obtained for differential pulse polarography in the concentration range from 2.0×10^{-7} M to 1.0×10^{-5} M as shown in Fig. 7. The sensitivity of the solvent extraction differential pulse polarographic determination of uranium is fifty times as high as that of the DC polarographic method. The determination limit of the DC polarographic technique is almost equivalent to those of the extraction colorimetry[6,8] and the conventional extraction polarography.[2]

It can be concluded that the proposed method for the determination of uranium (VI) using differential pulse polarography after solvent extraction is one hundred times more sensitive than the conventional methods.

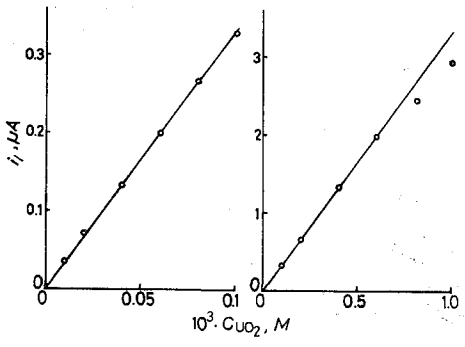

Fig. 6. Calibration curves of uranium (VI) in DC polarographic method.

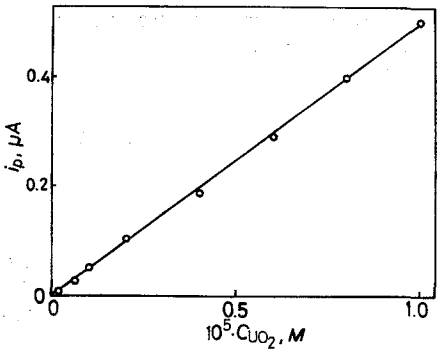

Fig. 7. Calibration curve of uranium (VI) in differential pulse polarography.
Conditions are the same as those in Fig. 5

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